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(54) **NOUVEAUX MATERIAUX POUR ELECTRODES DE TYPE A INSERTION DE LITHIUM, A BASE DE DERIVES DE TETRAOXYANIONS, AVEC STRUCTURE D'OLIVINE**

(54) **NEW LITHIUM INSERTION ELECTRODE MATERIALS BASED ON TETRAOXYANIONS DERIVATIVES WITH OLIVINE STRUCTURE**

(57) Matériau pour électrode positive de type à insertion de lithium, possédant une structure d'olivine, à base de dérivés du fer ou du manganèse, dont la formule générale est $Li_{x-y}M_{1-(y+d+t+q+r)}D_dT_tQ_qR_r[PO_4]_{1-(p+s+v)}[SO_4]_p[SIO_4]_s[VO_4]_v$, où : M représente Fe^{2+} ou Mn^{2+} ou un mélange des deux; D représente un métal au niveau d'oxydation +2, choisi parmi Mg^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+} et Ti^{2+}; T représente un métal au niveau d'oxydation +3, choisi parmi Al^{3+}, Ti^{3+}, Cr^{3+}, Fe^{3+}, Mn^{3+}, Ga^{3+}, Zn^{2+} et V^{3+}; Q représente un métal au niveau d'oxydation +4, choisi parmi Ti^{4+}, Ge^{4+}, Sn^{4+} et V^{4+}. R représente un métal au niveau d'oxydation +5, choisi parmi V^{5+}, Nb^{5+} et Ta^{5+}. Tous les M, D, T, Q et R sont des éléments se trouvant dans des sites octaédrique; v est le coefficient stoechiométrique pour le V^{5+} situé dans des sites tétraédrique. Les coefficients stoechiométriques x, y, d, t, q, r, p, s, v sont tous compris entre zéro et un, et l'un au moins des coefficients y, d, t, q, r, p, s et v est différent de zéro. Les autres conditions sont les suivantes : $0 \leq x \leq 1$ $y + d + t + q + r \leq 1$ $p + s + v \leq 1$ $3 + s - p = x - y + t + 2q + 3r$, où x est le degré d'intercalation pendant le fonctionnement du matériau d'électrode.

(57) A lithium insertion-type positive electrode materials having an olivine structure based on iron or manganese derivatives, whose general formula is: $Li_{x-y}M_{1-(y+d+t+q+r)}D_dT_tQ_qR_r[PO_4]_{1-(p+s+v)}[SO_4]_p[SIO_4]_s[VO_4]_v$ where: M represents Fe^{2+} or Mn^{2+} or mixtures thereof; D represents a metal in the +2 oxidation state, chosen among: Mg^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Ti^{2+}; T represents a metal in the +3 oxidation state, chosen among: Al^{3+}, Ti^{3+}, Cr^{3+}, Fe^{3+}, Mn^{3+}, Ga^{3+}, Zn^{2+}, V^{3+} Q represents a metal in the +4 oxidation state, chosen among: Ti^{4+}, Ge^{4+}, Sn^{4+}, V^{4+}. R represents a metal in the +5 oxidation state, chosen among: V^{5+}, Nb^{5+}, Ta^{5+}. All M, D, T, Q, R, are elements residing in octahedral sites; v is the stoichiometric coefficient for V^{5+} residing in tetrahedral sites. The stoichiometric coefficients x, y, d, t, q, r, p, s, v are all comprised between zero and one with at least one among of the y, d, t, q, r, p, s and v coefficients differing from zero. Other conditions are: $0 \leq x \leq 1$ $y + d + t + q + r \leq 1$ $p + s + v \leq 1$ $3 + s - p = x - y + t + 2q + 3r$ where x is the degree of intercalation during operation of the electrode material.

ABSTRACT

A lithium insertion-type positive electrode materials having an olivine structure based on iron or manganese derivatives, whose general formula is:

$$Li_{x+y} M_{1-(y+d+t+q+r)} D_d T_t Q_q R_r [PO_4]_{1-(p+s+v)} [SO_4]_p [SiO_4]_s [VO_4]_v$$

where:

M represents Fe^{2+} or Mn^{2+} or mixtures thereof;

D represents a metal in the +2 oxidation state, chosen among: Mg^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Ti^{2+};

T represents a metal in the +3 oxidation state, chosen among: Al^{3+}, Ti^{3+}, Cr^{3+}, Fe^{3+}, Mn^{3+}, Ga^{3+}, Zn^{2+}, V^{3+}

Q represents a metal in the +4 oxidation state, chosen among: Ti^{4+}, Ge^{4+}, Sn^{4+}, V^{4+}.

R represents a metal in the +5 oxidation state, chosen among: V^{5+}, Nb^{5+}, Ta^{5+}.

All M, D, T, Q, R, are elements residing in octahedral sites; v is the stoichiometric coefficient for V^{5+} residing in tetrahedral sites.

The stoichiometric coefficients x, y, d, t, q, r, p, s, v are all comprised between zero and one with at least one among of the y, d, t, q, r, p, s and v coefficients differing from zero. Other conditions are:

$$\left|\begin{array}{l} 0 \leq x \leq 1 \\ y + d + t + q + r \leq 1 \\ p + s + v \leq 1 \\ 3 + s - p = x - y + t + 2q + 3r \end{array}\right.$$

where x is the degree of intercalation during operation of the electrode material.

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NEW LITHIUM INSERTION ELECTRODE MATERIALS BASED ON TETRAOXYANIONS DERIVATIVES WITH OLIVINE STRUCTURE

Description of prior art:

Electrode materials with the olivine structure $LiFePO_4$ (triphyllilte) and the quasi-isomorphous delithiated material $\square FePO_4$ have the advantage of an operating voltage of 3.5 V vs. Li^+/Li°, i.e in the stability window of both liquid and polymer electrolytes with a flat discharge (lithium intercalation) plateau. The materials are however limited both by slow Li^+ diffusion kinetics and low electronic conductivity. The absence of non-stoichiometry or mutual miscibility for both phases ($LiFePO_4$ and $\square FePO_4$) provides an explanation for these undesirable properties. The materials obtained by partial substitution of iron by manganese behave similarly.

Description of the invention:

In the present invention, the pristine olivine structure of $LiMPO_4$ (M = Fe or Mn or their solid solutions) is modified either or both on the anionic and cationic sites, by aliovalent or isocharge substitutions, to provide better lithium ion diffusivity and electronic conductivity. For instance, these substitutions allows for the coexistence of iron or manganese in two different oxidation states in the same phase, or introduce specific interations with other elements having redox levels close to those of Fe and Mn (e.g.: $Fe^{2+}/Ti^{4+} \Leftrightarrow Fe^{3+}/Ti^{3+}$, $Mn^{2+}/V^{5+} \Leftrightarrow Mn^{3+}/V^{4+}$ etc...) both of which are favorable to electronic conductivity, while disorder on the anionic site provides preferential diffusion sites for Li^+. Along the same line, partial substitution of phosphorus by vanadium and to some extend by silicon, increases the lattice parameters, thus the size of the bottlenecks which tends to slow diffusion. The formation of non-stiochiometry domains with mixed valence states and/or transition-metal mediated electron hopping as well as partial substitution of phosporus sites differentiates this new family of compounds from the $LiFePO_4/\square FePO_4$ in which the totality of Fe (Mn) in either in the +II or +III oxidation state.

CLAIMS

1) A lithium insertion-type positive electrode materials having an olivine structure based on iron or manganese derivatives, whose general formula is:

$$Li_{x+y}M_{1-(y+d+t+q+r)}D_dT_tQ_qR_r[PO_4]_{1-(p+s+v)}[SO_4]_p[SiO_4]_s[VO_4]_v$$

where:

M represents Fe^{2+} or Mn^{2+} or mixtures thereof;

D represents a metal in the +2 oxidation state, chosen among: Mg^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Ti^{2+};

T represents a metal in the +3 oxidation state, chosen among: Al^{3+}, Ti^{3+}, Cr^{3+}, Fe^{3+}, Mn^{3+}, Ga^{3+}, Zn^{2+}, V^{3+}

Q represents a metal in the +4 oxidation state, chosen among: Ti^{4+}, Ge^{4+}, Sn^{4+}, V^{4+}.

R represents a metal in the +5 oxidation state, chosen among: V^{5+}, Nb^{5+}, Ta^{5+}.

All M, D, T, Q, R, are elements residing in octahedral sites; v is the stoichiometric coefficient for V^{5+} residing in tetrahedral sites.

The stoichiometric coefficients x, y, d, t, q, r, p, s, v are all comprised between zero and one with at least one among of the y, d, t, q, r, p, s and v coefficients differing from zero. Other conditions are:

$$\left|\begin{array}{l} 0 \le x \le 1 \\ y + d + t + q + r \le 1 \\ p + s + v \le 1 \\ 3 + s - p = x - y + t + 2q + 3r \end{array}\right.$$

where x is the degree of intercalation during operation of the electrode material.

2) Electrical generator having a least one positive and one negative electrode characterized in that at least one positive electrode contains a material according to claim 1 and at least one negative electrode is a source of lithium ion at a high chemical activity.

3) Electrical generator according to claim 2 characterized in that the negative electrode is metallic lithium, a lithium alloy, a lithium-carbon intercalation compound, a lithium-titanium spinel $Li_{1+x+z}Ti_{2-x}O_4$ ($0 \le x \le 1/3$; $0 \le z \le 1-2x$) and its solid solutions with other spinels, or a lithium-transition metal mixed nitride of antifluorite or related structures and mixtures thereof.

4) Electrical generator according to claim 2 characterized in that a conductive additive is present in the positive electrode.

5) Electrical generator according to claim 2 characterized in that the conductive additive in the positive electrode material is carbon.

6) Electrical generator according to claim 2 characterized in that the positive electrode contains in addition to the materials of claim 1 an intercalation material with fast diffusion kinetics

7) Electrical generator according to claim 2 characterized in that the positive electrode contains in addition to the materials of claim 1 an intercalation material with fast diffusion kinetics like a lamellar dichalcognenide, a vanadium oxide VO_x ($2.1 \leq x \leq 2.5$) or a Nasicon-related material, like $Li_3Fe_2(PO4)_3$ or $Li_{3-x}Fe_{2-x}Ti_x(PO_4)_3$.

8) Electrical generator according to claims 2 to 5 characterized in that the the positive electrodes contains a polymeric binder.

9) Electrical generator according to claims 2 to 5 characterized in that the polymeric binder is an homopolymer or copolymer of tetrafluoroethylene or an ethylene-propylene-diene terpolymer.

10) Electrical generator according to claim 2 to 6 characterized in that the polymeric binder possesses ionic conductivity

11) Electrical generator according to claim 7 characterized in that the polymeric binder is a polyether crosslinked or not and dissolving a salt, the cation of which is at least in part Li^+.

12) Electrical generator according to claim 7 characterized in that the polymeric binder is swollen by an aprotic solvent and contains a salt, the cation of which is at least in part Li^+.

13) Electrical generator according to claim 9 characterized in that the polymeric binder is a polyether, a polyester, a methylmethacrylate-based polymer, an acrylonitrile-based polymer, a vinylidene fluoride-based polymer.

14) Electrical generator according to claim 9 characterized in that the approtic solvent is ethylene carbonate, propylene carbonate, dimethylcarbonate, diethylcarbonate, methyl-ethylcarbonate, γ-butyrolactone, a tetraalkylsufamide, a dialkyether of a mono-, di-, tri-, tetra- or higher oligo-ethylene glycols of molecular weight lower or equal to 2000, and mixtures thereof.

15) variable optical transmission device constructed from transparent semi-conductor coated glass or plastic and two electrodes separated by a solid or gel electrolytes, characterized in that at least one of the electrode contain a material according to claim 1.

16) variable optical transmission device according to claim 12 characterized in that at least one of the electrode is obtained by laying a thin film of material according to claim 1 on a transparent semi-conductor coated glass or plastic by a vaccum deposition technique, sputtering, or from a sol-gel precursor.